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ABSTRACT

The initial assignment of Project 6502 was to develop analytical methods for measuring the MS and SS deliveries of selected components which have been targeted by the Surgeon General as being important contributors to the irritation of environmental tobacco smoke (ETS). The following methods were developed, beginning in the 4th quarter, 1987:

1) MS/SS total ammonia (NH_3 + NH_4^+) by ion chromatography (IC);
2) MS/SS benzene and toluene by gas chromatography (GC);
3) Puff-by-puff MS/SS acrolein by tunable diode laser (TDL) spectroscopy;
4) MS/SS formaldehyde, acetaldehyde, acrolein, and butyraldehyde by high performance liquid chromatography (HPLC) using DNPH derivatives.
5) The puff-by-puff MS/SS gaseous ammonia (NH_3) TDL procedure was used also in the evaluation.

The above methods were used to measure the MS and SS deliveries for six cigarette models, consisting of a control (without) and test (with $Mg(OH)_2$ paper) at 17, 20 and 24.8mm circumference. These models were selected for evaluation in discussions between Chemical Research, Cigarette Technology, and Analytical Research personnel. A summary of the important conclusions obtained from this study is given below:

1) The $Mg(OH)_2$ cigarettes for all three circumference models showed ~10% increase in the SS gaseous and total ammonia deliveries relative to their respective controls.

2) There was an increase in the MS gaseous NH_3 deliveries and a slight decrease in the MS total ammonia deliveries of the test models compared with the respective controls. Therefore, it appears that the $Mg(OH)_2$ paper causes a slight increase in the NH_3/NH_4^+ distribution in MS smoke.

3) The $Mg(OH)_2$ models delivered 5 to 10% more benzene and 5 to 10% less toluene to the SS smoke compared to the respective controls. The SS toluene/benzene ratio showed a 10% decrease for the $Mg(OH)_2$ models compared to their respective controls. This "chemical theromometer" suggests that there may be an increase in the tobacco pyrolytic temperature for the $Mg(OH)_2$ model cigarettes.

4) Both benzene and toluene showed increased MS deliveries, on a per puff basis, for cigarettes with the $Mg(OH)_2$ paper compared with their respective controls. The increase in benzene was ~25% for all three circumferences, while the toluene MS deliveries increased 10, 20 and 40% for the 24.8 mm, 20 mm and 17 mm $Mg(OH)_2$ models, respectively.

5) SS formaldehyde deliveries of the $Mg(OH)_2$ models showed reductions ranging from 20 to 25% compared to the controls.

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6) SS acetaldehyde deliveries were the same for the controls and the $Mg(OH)_2$ models for both 20 and 24.8mm circumference.

7) SS acrolein deliveries of the $Mg(OH)_2$ models showed a 15% increase relative to the controls. Similar trends were observed using the acrolein puff-by-puff TDL procedure.

8) The $Mg(OH)_2$ test samples showed a ~25% reduction in per cigarette MS acrolein deliveries compared to their respective controls. On a per puff basis, the reduction was less.

9) The SS total aldehyde deliveries of the $Mg(OH)_2$ models were similar to their respective control. Acetaldehyde accounted for ~50% of the total.

10) Based on mg/g, the magnitude of the sum of the SS deliveries for these four aldehydes was similar to that determined for total ammonia. Combined, they contributed >15 mg/g to the SS smoke of a conventional blended cigarette.

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I. OBJECTIVE

The purpose of this report was to summarize the mainstream (MS) and sidestream (SS) data obtained on cigarette models consisting of cigarette paper with and without $Mg(OH)_2$ at 17, 20 and 24.8 mm circumference using analytical methods newly developed within Project 6502.

II. INTRODUCTION

The initial assignment of Project 6502 was to develop analytical methods for measuring the MS and SS deliveries of selected components which have been targeted by the Surgeon General as being important contributors to the irritation of environmental tobacco smoke (ETS) [1]. Table I below lists the major irritants in ETS, their MS concentrations, the SS/MS ratios, and levels in smoky air, as given in the 1986 Surgeon General's report [1].

TABLE I

Major Irritants in ETS as Reported by the Surgeon General

Irritant	MS (per cigt.)	SS/MS Ratio	Smoky Air
acrolein	10-140µg	10-20	6-120ppb
ammonia	10-500µg	44-100	1000-4580ppb
formaldehyde	20-90µg	~50	30-60ppb
nitrogen oxides	16-600µg	4.7-50	1-370ppb NO 0-50ppb NO_2
phenol	20-150µg	2.6	7.4-115µg/m^3
pyridine	32µg	10	NA
sulfur dioxide	1-75ppb	NA	1-69ppb
toluene	108µg	5.6	0.04-1.04mg/m^3
respirable particles	0.1-40mg	1.3-1.9	55-962mg/m^3

NA = not available

Data in Table I are shown only for reference. An assessment of the accuracy is not the focus of this report. Components to be measured were selected from this list and additional components were measured as well because, for some procedures, they could be obtained simultaneously. The following methods were developed, beginning in the 4th quarter, 1987 by personnel in Project 6502:

1) MS/SS total ammonia (NH_3 + NH_4^+) by ion chromatography (IC);
2) MS/SS benzene and toluene by gas chromatography (GC);
3) Puff-by-puff MS/SS acrolein by tunable diode laser (TDL) spectroscopy [2];
4) MS/SS formaldehyde, acetaldehyde, acrolein, and butyraldehyde by high performance liquid chromatography (HPLC) using DNPH derivatives.

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The puff-by-puff MS/SS gaseous ammonia (NH_3) TDL procedure was used also in the evaluation [3].

The above methods were used to measure the MS and SS deliveries for six cigarette models, consisting of a control (without) and test (with $Mg(OH)_2$ paper) at 17, 20 and 24.8mm circumference. These models were selected for evaluation in discussions between Chemical Research, Cigarette Technology, and Analytical Research personnel. The specifications of the cigarettes and the analytical data obtained for each model were given in a memo by B. Goodman and a copy is attached in the Appendix to this report for reference [4]. The cigarette models were received already conditioned and screened for RTD. Since the models varied considerably in filler weights, the SS data were calculated based on filler and paper consumed (mg/g), as well as the normal mg/cigt. basis. All cigarettes were smoked to a 35mm butt length, and unless otherwise stated, a rectangular glass SS chamber, having a flow rate of 2.3 to 2.5 L/min., was employed. All of the data have been reported either in memos, and/or Project monthly reports [5-8].

III. RESULTS AND DISCUSSION

A. Gaseous and Total Ammonia Deliveries [5,6]

The MS gaseous and total ammonia deliveries are given in Table II.

Table II

MS Gaseous (TDL) and Total Ammonia (IC) Deliveries

Sample	Gaseous NH_3 (µg/cigt.)	Total Ammonia (µg/cigt.)	% NH_3 in Total
Control-17mm (D7CZE)	2.0	21.2	9
Test-17mm (D7CZD)	2.2	20.1	11
Control-20mm (D7CZG)	1.9	24.3	8
Test-20mm (D7CZF)	2.2	20.4	11
Control-24.8mm (D7CZH)	2.4	27.5	9
Test-24.8mm (D7CZI)	2.6	25.4	10
Monitor 24	2.1	31.3	7

The total ammonia deliveries listed above are obtained from averaging the results using the method by G. Vilcins [9] with the results using the MS/SS method developed by Randolph [6]. The data show a slight increase in the gaseous NH_3 deliveries and a slight decrease in the total ammonia deliveries of the test models compared with the respective controls. Therefore, it appears that the $Mg(OH)_2$ paper caused a slight change in the NH_3/NH_4^+ distribution in MS smoke. This distribution ratio is sensitive to pH and/or moisture differences of the cigarette smoke.

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The SS gaseous and total ammonia deliveries are given in Table III.

TABLE III

SS Gaseous (TDL) and Total Ammonia (IC) Deliveries

Sample	Gaseous NH_3		Total Ammonia		SS/MS Ratio
	mg/cigt.	mg/g	mg/cigt.	mg/g	(per cigt.)
Control-17mm (D7CZE)	3.4	7.9	4.0	9.5	190
Test-17mm (D7CZD)	4.1	8.4	4.6	9.6	230
Control-20mm (D7CZG)	4.7	8.3	5.6	10.1	230
Test-20mm (D7CZF)	5.0	8.3	5.9	9.8	290
Control-24.8mm (D7CZH)	8.0	9.1	8.7	10.2	390
Test-24.8mm (D7CZI)	8.7	9.4	9.9	11.4	470
Monitor 24	5.8	8.5	6.9	10.0	230

The results showed a definite trend of higher SS ammonia deliveries due to the $Mg(OH)_2$ paper for all three circumference models. The increase of ~10% was observed by both the TDL gaseous and the IC total ammonia methods [5,6]. The SS/MS ratio values were obtained using the total ammonia per cigt. data. The ratios increased with increasing circumference and were higher for the $Mg(OH)_2$ models compared to the controls. However, the percent increase of the $Mg(OH)_2$ models relative to their respective controls was the same for each circumference. This supports the observation discussed above concerning the slight increase in the NH_3/NH_4^+ distribution in the MS smoke. Both calculations suggest that the pH of the smoke is more alkaline for the $Mg(OH)_2$ models.

The SS/MS ratio values reported here are two to four times that given in Table I. However, based on previous studies conducted in the TDL laboratory, the upper range in MS ammonia deliveries reported in Table I is unreasonably high for normal commercial cigarettes [3]. In any case, ammonia should be considered an important contributor to ETS because of its sensory properties and the quantity present in SS smoke. Even though fundamental studies are lacking, it appears unlikely that the small increases in SS ammonia deliveries observed for the $Mg(OH)_2$ models would result in a more objectionable SS relative to odor and irritancy.

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B. Benzene and Toluene Deliveries [7]

The benzene and toluene MS deliveries for the six model cigarettes are given in Table IV.

TABLE IV

MS Benzene and Toluene Deliveries

Sample	Benzene		Toluene	
	(µg/cigt)	(µg/puff)	(µg/cigt)	(µg/puff)
Control-17mm (D7CZE)	40	5.1	62	7.9
Test-17mm (D7CZD)	53	6.5	92	11.2
Control-20mm (D7CZG)	66	6.7	100	10.1
Test-20mm (D7CZF)	65	8.1	97	12.1
Control-24.8mm (D7CZH)	90	7.3	150	12.2
Test-24.8mm (D7CZI)	97	9.2	145	13.6
Monitor 24	60	6.5	105	11.5

Since the cigarettes vary considerably in puff counts, comparisons should be made using the per puff deliveries. Both benzene and toluene showed increased MS deliveries for cigarettes with the $Mg(OH)_2$ paper compared with their respective controls. The increase in benzene was ~25% for all three circumferences, while the toluene MS deliveries increased 10, 20 and 40% for the 24.8 mm, 20 mm and 17 mm $Mg(OH)_2$ models, respectively. In regards to the effect of circumference on the MS benzene deliveries, a reduction of 30% was achieved for the 17 mm control compared to the 24.8 mm control. A 35% reduction was obtained in the toluene MS delivery for these two models. The SS deliveries for benzene and toluene are given in Table V.

TABLE V

SS Deliveries for Benzene and Toluene

Sample	Benzene Delivery		Toluene Delivery	
	(µg/cigt)	(µg/g)	(µg/cigt)	(µg/g)
Control-17mm (D7CZE)	190	460	415	1000
Test-17mm (D7CZD)	225	480	435	920
Control-20mm (D7CZG)	250	460	540	980
Test-20mm (D7CZF)	295	490	555	930
Control-24.8mm (D7CZH)	350	400	800	920
Test-24.8mm (D7CZI)	410	450	865	950
Monitor 24	280	410	635	930

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For all three $Mg(OH)_2$ models, the benzene SS deliveries were greater than their respective controls. The magnitude of the higher deliveries can be assessed more accurately by comparing the deliveries based on µg/g than on the per cigt. values. The increases were only 5 to 10% but this was observed for all three models. In the case of toluene, the SS deliveries (ug/cigt. and µg/g) did not show the clear pattern as was observed for the benzene data. However, the best comparison would be using the µg/g values. These data showed that the toluene SS deliveries for the 17mm and 20 mm $Mg(OH)_2$ models were reduced by 5 to 10% compared with their respective controls. The 24.8 mm $Mg(OH)_2$ model delivered 950 µg/g compared to 920 µg/g for the control. The weight difference between the control and $Mg(OH)_2$ model for the 24.8 mm circumference was much greater than for the other two circumference model samples (see Appendix). The overall trend, however, suggests that the cigarettes having $Mg(OH)_2$ paper deliver 5 to 10% more benzene and 5 to 10% less toluene to the SS(µg/g) compared to their respective controls.

In regards to the effect of circumference on the SS benzene and toluene deliveries (µg/g), it appeared that similar results are obtained for the 17 mm and 20 mm controls, as well as the 17 mm and 20 mm $Mg(OH)_2$ models. These smaller circumference models delivered 10 to 15% more benzene in the SS (µg/g) compared to the 24.8 mm circumference models and this was observed for the controls as well as the $Mg(OH)_2$ samples. For the above comparisons using the toluene SS delivery (µg/g), the 10 to 20% increase was only observed for the control models. The trend was not observed with the $Mg(OH)_2$ models. The SS/MS ratios for benzene and toluene are given in Table VI.

TABLE VI

SS/MS Ratios for Benzene and Toluene

Sample Description	Benzene SS/MS Ratio	Toluene SS/MS Ratio
Control - 17mm (D7CZE)	5	7
Test - 17mm (D7CZD)	4	5
Control - 20 mm (D7CZG)	4	5
Test - 20 mm (D7CZF)	4	6
Control - 24.8mm (D7CZH)	4	5
Test - 24.8mm (D7CZI)	5	6
Monitor 24	5	6

The benzene SS/MS ratios of the 20 and 24.8mm controls were similar and both are lower than that obtained for the 17mm control. This same trend was observed for the toluene ratios. The toluene SS/MS ratios reported for these models are similar to the value given in Table I.

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The differences observed in the SS benzene and toluene deliveries between the control and $Mg(OH)_2$ cigarettes were explored in greater detail for two reasons. First, even though the measured differences were relatively small (5 to 10%), the change was positive for benzene and negative for toluene. Therefore, by obtaining a ratio of the two deliveries for each cigarette model, the individual changes detected for benzene and toluene were combined to provide a more accurate assessment of the effect $Mg(OH)_2$ paper may have on the SS smoke delivery. Secondly, it has been shown by Johnson and co-workers that the toluene/benzene ratio determined in cigarette smoke is characteristic of the smoke formation temperature [10]. Therefore, these calculations may provide additional information important to understanding whether the smoke temperature is being affected by the $Mg(OH)_2$ paper. The calculated toluene/benzene ratios for MS and SS smoke for the six model cigarettes are given in Table VII.

TABLE VII

MS and SS Toluene/Benzene Ratios

Sample Description	MS Ratio (µg/cigt.)	SS Ratio (µg/g)
Control - 24.8 mm (D7CZH)	1.7	2.2
Test - 24.8 mm (D7CZI)	1.5	1.9
Control - 20 mm (D7CZG)	1.5	2.1
Test - 20 mm (D7CZF)	1.5	1.9
Control - 17 mm (D7CZE)	1.6	2.3
Test - 17 mm (D7CZD)	1.7	2.1
Monitor 24	1.8	2.3

While no pattern could be seen with the MS toluene/benzene ratios, the SS ratios showed a definite trend, in that the models having $Mg(OH)_2$ paper showed lower ratios than their respective controls. The magnitude of the decrease for the three models was ~10%. Based on the results of Johnson and co-workers, the lowering of the ratio indicated an increase in the tobacco pyrolytic temperature. Although static coal temperature measurements showed a 30°C decrease for cigarettes made with $Mg(OH)_2$ paper compared with controls, there were no clear differences observed in the dynamic coal temperature measurements [11]. Physical temperature measurements may not be sensitive or accurate enough to observe the pyrolytic temperature changes suggested by the "chemical thermometer" (toluene/benzene ratio data). Additional experiments would be required to verify these conclusions because the data were a result of one model system and also were based on five (5) determinations per sample.

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C. Puff-By-Puff Acrolein Deliveries [8]

The puff-by-puff MS acrolein deliveries measured using the TDL procedure are given in Table VIII.

TABLE VIII

MS Puff-by-Puff Acrolein Deliveries by TDL

Sample	Acrolein Delivery (µg/cigt.)	(µg/puff)
Control-17mm (D7CZE)	100	11.5
Test-17mm (D7CZD)	75	8.9
Control-20mm (D7CZG)	115	11.7
Test-20mm (D7CZF)	90	10.7
Control-24.8mm (D7CZH)	125	10.3
Test-24.8mm (D7CZI)	90	9.1
Monitor 24	115	12.0

The $Mg(OH)_2$ test samples showed ~25% reduction in per cigarette MS acrolein deliveries compared to their respective controls. On a per puff basis, the reduction was less. The range in the per puff deliveries for these models were similar to those obtained for the per puff acrolein deliveries which were measured for bright, burley and oriental tobaccos [12].

Cigarettes from the same population were analyzed for SS acrolein. The results of the SS acrolein deliveries are given in Table IX.

TABLE IX

Averaged SS Acrolein Deliveries for Circumference Model Cigarettes

Sample	Acrolein Delivery (µg/cigt)	(µg/g)	SS/MS Ratio (per cigt.)
Control-17mm (D7CZE)	360	870	4
Test-17mm (D7CZD)	430	890	6
Control-20mm (D7CZG)	460	820	4
Test-20mm (D7CZF)	480	820	5
Control-24.8mm (D7CZH)	680	780	5
Test-24.8mm (D7CZI)	780	860	8
Monitor 24	570	840	5

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The SS acrolein per cigarette deliveries were difficult to compare in this data set due to the significant differences in the burn times and tobacco weights. However, the $Mg(OH)_2$ test samples were slightly higher than their respective controls by ~10%. The value of 840 µg/g for the Monitor 24 was in good agreement with the values obtained for the six models (780 to 890 µg/g). This suggested that the SS acrolein deliveries were not greatly affected by the circumference but the use of $Mg(OH)_2$ paper did increase the delivery somewhat for these models studies. The SS/MS ratio values were all higher for the $Mg(OH)_2$ models and generally increased as the circumference increases. The SS/MS ratios reported for acrolein in Table I appear to be on the high side compared to the data obtained in this study for normal blended cigarettes.

D. MS/SS Aldehyde Deliveries by HPLC Using DNPH Derivitives [13]

The MS/SS deliveries of formaldehyde, acetaldehyde, acrolein and butyraldehyde were measured using DNPH dervitization followed by separation and quantitation by HPLC. A modified rectangular glass SS chamber, heated to ~50°C, was used with a flow rate of 2 L/min. The MS deliveries are given in Table X.

TABLE X

MS Aldehyde Deliveries by HPLC Using DNPH Derivitives

Sample	Formaldehyde		Acetaldehyde		Acrolein		Butyraldehyde	
	µg/cig	µg/puff	µg/cig	µg/puff	µg/cig	µg/puff	µg/cig	µg/puff
Control-17mm (D7CZE)	40	6.0	585	85	65	9.0	3.0	0.5
Test-17mm (D7CZD)	13	2.0	520	70	35	4.5	8.0	1.0
Control-20mm (D7CZG)	55	7.0	860	115	100	13.1	33.0	4.4
Test-20mm (D7CZF)	20	3.0	700	100	55	7.6	33.0	5.0
Control-24.8mm (D7CZH)	18	1.9	730	80	80	8.5	30.0	3.2
Test-24.8mm (D7CZI)	18	2.2	860	100	65	7.6	40.0	4.9
Monitor 24	43	5.4	850	105	105	14.2	54.0	6.7

The MS formaldehyde, acetaldehyde and acrolein deliveries were lower for the $Mg(OH)_2$ 17mm and 20mm models compared to their respective controls. This same trend was observed for the MS acrolein deliveries determined using the puff-by-puff TDL procedure (see Table VIII). The MS formaldehyde and acrolein deliveries are within the ranges reported in Table I. The SS deliveries for formaldehyde, acetaldehyde, acrolein and butyraldehyde are listed in Table XI.

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TABLE XI

SS Aldehyde Deliveries by HPLC Using DNPH Derivitives

Sample	Formaldehyde		Acetaldehyde		Acrolein		Butyraldehyde	
	µg/cig	µg/g	µg/cig	µg/g	µg/cig	µg/g	µg/cig	µg/g
Control-17mm (D7CZE)	770	1880	1500	3650	450	1100	165	400
Test-17mm (D7CZD)	700	1450	2000	4150	630	1300	130	260
Control-20mm (D7CZG)	860	1530	1800	3250	430	775	340	610
Test-20mm (D7CZF)	630	1090	1880	3250	570	980	350	610
Control-24.8mm (D7CZH)	1600	1860	3650	4250	800	930	590	690
Test-24.8mm (D7CZI)	1260	1400	3850	4300	1020	1130	700	780
Monitor 24	1380	2035	2620	3850	640	940	500	740

The results showed that the SS acrolein deliveries followed the same trend observed using the puff-by-puff TDL procedure (see Table IX). The SS acrolein deliveries of the $Mg(OH)_2$ models showed ~15% increase relative to their respective controls. However, SS formaldehyde deliveries of the $Mg(OH)_2$ models showed 20 to 25% reductions compared to their respective controls. Except for the 17mm models, the SS acetaldehyde and butyraldehyde deliveries were not affected significantly by the $Mg(OH)_2$ paper. Since the SS deliveries of the four aldehydes were not affected similarly by the $Mg(OH)_2$ paper, the sum of these four major aldehydes may not show a major difference compared to the respective controls. The SS total aldehyde delivery (based on both mg/cigt. and mg/g) and the individual SS/MS ratios (per cigt.) are listed in Table XII.

TABLE XII

SS Total Aldehyde Deliveries and SS/MS Ratios

Sample	Total Aldehydes		SS/MS Ratio			
	mg/cig	mg/g	Formaldehyde	Acetaldehyde	Acrolein	Butyraldehyde
Control-17mm (D7CZE)	2.9	7.1	50	4	18	55
Test-17mm (D7CZD)	3.5	7.0	18	2	7	16
Control-20mm (D7CZG)	3.4	5.9	30	3	11	10
Test-20mm (D7CZF)	3.4	6.2	16	2	4	10
Control-24.8mm (D7CZH)	6.6	7.7	70	4	16	19
Test-24.8mm (D7CZI)	6.8	8.0	90	5	10	17
Monitor 24	5.3	7.8	32	3	6	10

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The SS total aldehyde deliveries of the $Mg(OH)_2$ models were similar to their respective control. Acetaldehyde accounted for ~50% of the total. Based on mg/g, the magnitude of the sum of the SS deliveries for these four aldehydes was similar to that determined for total ammonia. Combined, they contributed >15 mg/g to the SS smoke of a conventional blended cigarette. Consequently, it would appear logical to make a synthetic mixture of these five compounds using concentrations similar to those reported in this study. Then the mixture could be evaluated at various dilutions using humidified air to determine the threshold level. In addition, the panelists could assess the impact of the odor and irritancy attributes of the mixture. The procedures developed by A. Kallianos and M. Jeltema using the aluminum environmental chamber could be used for this purpose. An assessment of the type of results obtained using this chamber has recently been reviewed [14].

The SS/MS ratios of formaldehyde ranged from 16 to 90, due mostly to the wide range measured in the MS (13 to 55 µg/cigt.). The SS/MS ratio for formaldehyde listed in Table I was ~50. This variation was not surprising since formaldehyde is such a highly reactive species. Work performed in the TDL laboratory demonstrated that several factors significantly influenced the MS formaldehyde delivery. These factors included the lighting technique, the flow through the cigarette, filter ventilation, moisture equilibration of the cigarette, and the density of the cigarette along the filler rod [15]. The temperature of the inlet lines of the experimental apparatus has a significant effect on the MS and SS formaldehyde deliveries as well [16,17]

IV. CONCLUSIONS

Methods were developed and used to evaluate the effect of circumference and $Mg(OH)_2$ paper on the MS/SS deliveries of gaseous and total ammonia, benzene and toluene, puff-by-puff acrolein, and DNPH derivitives of formaldehyde, acetaldehyde, acrolein, and butyraldehyde. A summary of the important conclusions obtained from this study is given below:

1) The $Mg(OH)_2$ cigarettes for all three circumference models showed ~10% increase in the SS gaseous and total ammonia deliveries relative to their respective controls.

2) There was an increase in the MS gaseous NH_3 deliveries and a slight decrease in the MS total ammonia deliveries of the test models compared with the respective controls. Therefore, it appears that the $Mg(OH)_2$ paper caused a slight increase in the NH_3/NH_4^+ distribution in MS smoke.

3) The $Mg(OH)_2$ models delivered 5 to 10% more benzene and 5 to 10% less toluene to the SS smoke compared to the respective controls. The SS toluene/benzene ratio showed a 10% decrease for the $Mg(OH)_2$ models compared to their respective controls. This "chemical theromometer" suggests that there may be an increase in the tobacco pyrolytic temperature for the $Mg(OH)_2$ model cigarettes.

4) Both benzene and toluene showed increased MS deliveries for cigarettes with the $Mg(OH)_2$ paper compared with their respective controls. The increase in benzene was ~25% for all three circumferences, while the toluene

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MS deliveries increased 10, 20 and 40% for the 24.8 mm, 20 mm and 17 mm $Mg(OH)_2$ models, respectively.

5) SS formaldehyde deliveries of the $Mg(OH)_2$ models showed reductions ranging from 20 to 25% compared to the controls.

6) SS acetaldehyde deliveries were the same for the controls and the $Mg(OH)_2$ models for both 20 and 24.8mm circumference.

7) SS acrolein deliveries of the $Mg(OH)_2$ models showed a 15% increase relative to the controls. Similar trends were observed using the puff-by-puff TDL procedure.

8) The $Mg(OH)_2$ test samples showed a ~25% reduction in per cigarette MS acrolein deliveries compared to their respective controls. On a per puff basis, the reduction was less.

9) The SS total aldehyde deliveries of the $Mg(OH)_2$ models were similar to their respective control. Acetaldehyde accounted for ~50% of the total.

10) Based on mg/g, the magnitude of the sum of the SS deliveries for these four aldehydes was similar to that determined for total ammonia. Combined, they contributed >15 mg/g to the SS smoke of a conventional blended cigarette.

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VI. ACKNOWLEDGEMENTS

The authors would like to thank B. Goodman and R. Comes for their suggestions as to the selection of the six cigarette models to evaluate.

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VII. APPENDIX

The Appendix contains the memo from B. Goodman listing the cigarette specifications and the analytical data performed by the CI Division for all six models.

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PHILIP MORRIS U.S.A.

INTER-OFFICE CORRESPONDENCE

Richmond, Virginia

To: Distribution

Date: 25 September, 1987

From: Barbro Goodman

Subject: CIGARETTES FOR ANALYTICAL SIDESTREAM RESEARCH

Based on discussions between Chemical Research, Analytical Research, and Cigarette Technology personnel, several cigarette models were designed specifically for research on sidestream smoke composition. The objective for the upcoming studies is to investigate the effect of cigarette circumference and Mg(OH)2 wrapper. In order to provide a matrix for the analyses, prototypes were made at three different circumferences (17 mm, 20 mm and 24.8 mm) each with a standard commercial wrapper (Kimberly-Clark 156) and with a 12% Mg(OH)2 wrapper. All the cigarettes were made from the same batch of tobacco in a nondiluted 100 mm filtered configuration.

The selected blend was the current project TRIM blend with standard production components. DBC Bright, DBC Burley, MT Oriental, RLTC and RL 150B was used. It contained no stems or expanded tobaccos, so that better looking ultra slim cigarettes could be produced. All samples had the same casing and aftercut system.

The Hauni lab max was used for all three circumferences. Cellulose acetate filters were made with widely varying efficiencies in an effort to keep the mainstream tar deliveries within reasonable levels. The tables attached to this memo give analytical data for each of the models. As can be seen in Table I, the 17 mm configuration gave extremely high RTD's for nonventilated cigarettes. This could have an effect on mainstream puffing to a greater extent than for a standard circumference cigarette. Ultra slim prototypes typically have RTD's above 6" water for 45 - 55% filter ventilation. The variability of the RTD was also greater for the slim cigarettes.

Tables II and III give the calculated differences in data for each circumference with the commercial and the low sidestream wrappers at standard circumference as controls.

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In addition to the circumference matrix, three other pairs of cigarettes will be investigated for sidestream deliveries of certain components. These cigarettes represent three different tar categories; full flavor, flavor low, and ultra low tar, all with the 12% $Mg(OH)_2$ wrapper. Each tar level has a commercial control companion. The mainstream deliveries for these cigarettes are shown in Tables IV, V, and VI.

It is also strongly recommended that a prototype with higher levels of $Mg(OH)_2$ (35-40%) in the wrapper utilizing 100% expanded tobaccos be analyzed. Selection of such a model is in progress.

Barbro Goodman

Distribution:

A. Kallianos
R. Comes
R. Fenner
R. Ferguson
P. Gauvin
R. Slagle
Central File

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TABLE I

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****************************************
CIGT DEV PROGRAMS - DELIVERY
DATE: 22-SEP-87 File: data.del sec 23
NOTES: ANALYTICAL RESEARCH MATRIX
****************************************
```

X8D7	CZH 156 25MM 4712	CZI MGO 25MM 4713	CZG 156 20MM	CZF MGO 20MM	CZE 156 17MM	CZD MGO 17MM
TPM	20.5	21.7	18.9	19.5	15.0	13.5
Nic.	1.37	1.28	1.26	1.18	0.84	0.67
Water	2.1	2.5	2.9	3.2	2.7	1.8
P.C.	11.0	8.9	9.2	7.8	7.8	7.8
TAR	17.02	17.90	14.71	15.17	11.50	11.00
Tpm/Puff	1.864	2.438	2.054	2.500	1.923	1.731
Nic/Puff	.1245	.1438	.1370	.1513	.1077	.0859
Water/Puff	.1918	.2831	.3185	.4038	.3410	.2346
Tar/Puff	1.547	2.011	1.599	1.945	1.474	1.410
Nic/tar	.0805	.0715	.0857	.0778	.0730	.0609
S.B.T.	8.6	8.5	7.4	7.2	6.6	7.0
PC/SBT	1.279	1.047	1.243	1.083	1.182	1.114
Gas PC	11.4	8.9	9.0	6.8	7.5	7.8
NO mg	0.38	0.43	0.30	0.30	0.21	0.25
CO mg	16.5	25.0	14.2	22.1	10.0	16.8
HCN mg	0.16	0.16	0.19	0.18	0.14	0.15
RCHO mg	1.03	1.19	0.91	0.92	0.66	0.72
NO/Puff	.0333	.0483	.0333	.0441	.0280	.0321
CO/Puff	1.447	2.809	1.578	3.250	1.333	2.154
HCN/Puff	.0140	.0180	.0211	.0265	.0187	.0192
RCHO/Puff	.0904	.1337	.1011	.1353	.0880	.0923
NO/TAR	.0215	.0240	.0208	.0227	.0190	.0227
CO/TAR	0.935	1.397	0.987	1.671	0.904	1.527
HCN/TAR	.0091	.0089	.0132	.0136	.0127	.0136
RCHO/TAR	.0584	.0665	.0632	.0696	.0597	.0655
NO/NIC	.2676	.3359	.2434	.2916	.2600	.3731
CO/NIC	11.62	19.53	11.52	21.48	12.38	25.07
HCN/NIC	.1127	.1250	.1541	.1750	.1733	.2239
RCHO/NIC	.7254	.9297	.7383	.8943	.8171	1.0746
Eq.OV %	13.6	13.7	13.6	13.5	13.5	13.5
Tob.wt mg	906	946	605	601	451	487
Ctob.wt mg	895	933	597	594	446	482
Filt.RTD mm	104	103	112	112	107	110
Tot.RTD mm	147	147	195	208	248	321
Ventil %	0.0	0.0	0.0	0.0	0.0	0.0
Rod Circ mm	24.8	24.8	20.0	20.0	17.0	17.1
Rod Len mm	71.5	71.5	71.5	71.5	71.5	71.5
Butt Len mm	35.0	35.0	35.0	35.0	35.0	35.0
Filt Len mm	27.0	27.0	27.0	27.0	27.0	27.0
Porosity sec	17	29	17	29	17	29
Filt.Eff %	N.A.	56.0	39.0	N.A.	N.A.	29.0
Rod Vol cc	3.499	3.499	2.276	2.276	1.644	1.664
Rod Density	0.259	0.270	0.266	0.264	0.274	0.293
DYN. COALTMP	957.0	954.0	959.0	978.0	933.0	966.0
STATIC TEMP.	648.0	622.0	648.0	643.0	662.0	646.0
CALC. MBR	58.00	61.00	45.00	46.00	38.00	38.50
MBR/CIRC.	2.350	2.480	2.260	2.310	2.220	2.270
CIGT.RTD IN.	5.80	5.80	7.70	8.20	9.80	12.60
VISIBILITY %	53.00	24.00	39.00	17.00	34.00	13.00

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CIGT DEV PROGRAMS - DELIVERY
DATE: 22-SEP-87 File: data.del sec 23
NOTES: ANALYTICAL RESEARCH MATRIX
% CHANGE: X8D7CZH IS CONTROL
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TABLE II

X8D7	CZH 156 25MM 4712	CZI MGO 25MM 4713	CZG 156 20MM	CZF MGO 20MM	CZE 156 17MM	CZD MGO 17MM
TPM	0%	5%	-8%	-5%	-27%	-35%
Nic.	0%	-7%	-9%	-14%	-39%	-52%
Water	0%	19%	38%	49%	26%	-14%
P.C.	0%	-20%	-17%	-30%	-30%	-30%
TAR	0%	5%	-14%	-11%	-33%	-36%
Tpm/Puff	0%	30%	10%	34%	3%	-8%
Nic/Puff	0%	15%	9%	21%	-14%	-32%
Water/Puff	0%	47%	66%	110%	77%	22%
Tar/Puff	0%	29%	3%	25%	-5%	-9%
Nic/tar	0%	-12%	6%	-4%	-10%	-25%
S.B.T.	0%	-2%	-14%	-17%	-24%	-19%
PC/SBT	0%	-19%	-3%	-16%	-8%	-13%
Gas PC	0%	-22%	-22%	-41%	-35%	-32%
NO mg	0%	13%	-22%	-22%	-45%	-35%
CO mg	0%	51%	-14%	33%	-40%	1%
HCN mg	0%	0%	18%	12%	-13%	-7%
RCHO mg	0%	15%	-12%	-11%	-36%	-31%
NO/Puff	0%	44%	0%	32%	-16%	-4%
CO/Puff	0%	94%	9%	124%	-8%	48%
HCN/Puff	0%	28%	50%	88%	32%	37%
RCHO/Puff	0%	47%	11%	49%	-3%	2%
NO/TAR	0%	11%	-4%	5%	-12%	5%
CO/TAR	0%	49%	5%	78%	-4%	63%
HCN/TAR	0%	-2%	45%	50%	39%	50%
RCHO/TAR	0%	13%	8%	19%	2%	12%
NO/NIC	0%	25%	-10%	8%	-3%	39%
CO/NIC	0%	68%	-1%	84%	6%	115%
HCN/NIC	0%	10%	36%	55%	53%	98%
RCHO/NIC	0%	28%	1%	23%	12%	48%
Eq.OV %	0%	0%	0%	-1%	-1%	-1%
Tob.wt mg	0%	4%	-34%	-34%	-51%	-47%
Ctob.wt mg	0%	4%	-34%	-34%	-51%	-47%
Filt.RTD mm	0%	-1%	7%	7%	2%	5%
Tot.RTD mm	0%	0%	32%	41%	68%	118%
Ventil %	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
Rod Circ mm	0%	0%	-20%	-20%	-32%	-32%
Rod Len mm	0%	0%	0%	0%	0%	0%
Butt Len mm	0%	0%	0%	0%	0%	0%
Filt Len mm	0%	0%	0%	0%	0%	0%
Porosity sec	0%	70%	0%	70%	0%	70%
Filt.Eff %	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
Rod Vol cc	0%	0%	-35%	-35%	-54%	-53%
Rod Density	0%	4%	2%	1%	5%	13%
DYN. COALTMP	0%	-1%	0%	2%	-3%	0%
STATIC TEMP.	0%	-5%	0%	-1%	2%	-1%
CALC. MBR	0%	5%	-23%	-21%	-35%	-34%
MBR/CIRC.	0%	5%	-4%	-2%	-6%	-4%
CIGT.RTD IN.	0%	0%	32%	41%	68%	117%
VISIBILITY %	0%	-55%	-27%	-68%	-36%	-76%

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CIGT DEV PROGRAMS - DELIVERY
DATE: 22-SEP-87 File: data.del sec 23
NOTES: ANALYTICAL RESEARCH MATRIX
% CHANGE: X8D7CZI IS CONTROL

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TABLE III

X8D7	CZH 156 25MM 4712	CZI MGO 25MM 4713	CZG 156 20MM	CZF MGO 20MM	CZE 156 17MM	CZD MGO 17MM
TPM	-6%	0%	-13%	-11%	-31%	-38%
Nic.	7%	0%	-2%	-8%	-35%	-48%
Water	-17%	0%	16%	24%	5%	-28%
P.C.	23%	0%	3%	-13%	-13%	-13%
TAR	-5%	0%	-18%	-16%	-36%	-39%
Tpm/Puff	-24%	0%	-16%	2%	-22%	-30%
Nic/Puff	-14%	0%	-5%	5%	-26%	-41%
Water/Puff	-33%	0%	12%	42%	20%	-18%
Tar/Puff	-24%	0%	-21%	-4%	-27%	-30%
Nic/tar	12%	0%	19%	8%	2%	-15%
S.B.T.	1%	0%	-13%	-16%	-23%	-18%
PC/SBT	22%	0%	18%	3%	12%	6%
Gas PC	28%	0%	1%	-24%	-16%	-13%
NO mg	-12%	0%	-31%	-31%	-52%	-42%
CO mg	-34%	0%	-44%	-12%	-60%	-33%
HCN mg	0%	0%	18%	12%	-13%	-7%
RCHO mg	-14%	0%	-24%	-23%	-45%	-40%
NO/Puff	-32%	0%	-32%	-9%	-43%	-34%
CO/Puff	-49%	0%	-44%	15%	-53%	-24%
HCN/Puff	-22%	0%	17%	47%	3%	6%
RCHO/Puff	-33%	0%	-25%	1%	-35%	-31%
NO/TAR	-11%	0%	-14%	-6%	-21%	-6%
CO/TAR	-34%	0%	-30%	19%	-36%	9%
HCN/TAR	1%	0%	47%	52%	41%	52%
RCHO/TAR	-13%	0%	-5%	4%	-11%	-2%
NO/NIC	-21%	0%	-28%	-14%	-23%	11%
CO/NIC	-41%	0%	-42%	9%	-37%	28%
HCN/NIC	-10%	0%	23%	39%	38%	79%
RCHO/NIC	-22%	0%	-21%	-4%	-13%	15%
Eq.OV %	-1%	0%	-1%	-2%	-2%	-2%
Tob.wt mg	-5%	0%	-37%	-37%	-53%	-49%
Ctob.wt mg	-5%	0%	-37%	-37%	-53%	-49%
Filt.RTD mm	0%	0%	8%	8%	3%	6%
Tot.RTD mm	0%	0%	32%	41%	68%	118%
Ventil %	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
Rod Circ mm	0%	0%	-20%	-20%	-32%	-32%
Rod Len mm	0%	0%	0%	0%	0%	0%
Butt Len mm	0%	0%	0%	0%	0%	0%
Filt Len mm	0%	0%	0%	0%	0%	0%
Porosity sec	-42%	0%	-42%	0%	-42%	0%
Filt.Eff %	N.A.	0%	-31%	N.A.	N.A.	-49%
Rod Vol cc	0%	0%	-35%	-35%	-54%	-53%
Rod Density	-5%	0%	-2%	-3%	1%	8%
DYN. COALTMP	0%	0%	0%	2%	-3%	1%
STATIC TEMP.	4%	0%	4%	3%	6%	3%
CALC. MBR	-5%	0%	-27%	-25%	-38%	-37%
MBR/CIRC.	-6%	0%	-9%	-7%	-11%	-9%
CIGT.RTD IN.	0%	0%	32%	41%	68%	117%
VISIBILITY %	120%	0%	62%	-30%	41%	-46%

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TABLE IV

Comments:PROJECT STUDIO; FULL FLAVOR FILTER CHANGE; 12-15mg TAR.

	Black T5, N7 DKP MgO	Black C9, G5 DKQ Control
Smoke		
Butt Length, mm	28	28
FTC Tar, mg/cigt.	9.6	15.1
TPM, mg/cigt.	11.6	19.7
Nicotine, mg/cigt.	0.81	1.16
Water, mg/cigt.	1.26	3.45
Puffs/Cigt.	9.2	9.4
Filtration Eff., %	54	47
CO, mg/cigt.	12.3	13.4
NO, mg/cigt.	0.18	0.27
HCN, mg/cigt.	0.10	0.17
RCHO, mg/cigt.	0.56	0.70
Cigarette		
Static Burn Time, min	8.0	8.2
Circumference, mm	24.9	25.0
Diameter, mm	7.9	7.9
Paper		
Porosity, sec.	27	19
Filter		
RTD, mm of H2O	97	73
Tipping Paper Length, mm	25	25
Filler		
Wt. of Tob., g (12.5% O.V.)	0.727	0.734
Oven Volatiles, %	13.6	14.0
Cigarette		
Ventilation, %	39	17
RTD, inches	4.8	4.1

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TABLE V

Comments:PROJECT STUDIO; FLAVOR - LOW FS O/C PANEL; 8-12mg TAR

	Black D6 DKI	Black G8 DKJ
Smoke		
Butt Length, mm	35	35
FTC Tar, mg/cigt.	10.3	7.0
TPM, mg/cigt.	12.5	8.4
Nicotine, mg/cigt.	0.78	0.59
Water, mg/cigt.	1.51	0.78
Puffs/Cigt.	8.6	7.5
Filtration Eff., %	53	
CO, mg/cigt.	10.4	11.3
NO, mg/cigt.	0.25	0.20
HCN, mg/cigt.	0.12	0.08
RCHO, mg/cigt.	0.61	0.50
Use Phase Puff Count		
Cigarette		
Static Burn. Time, min	8.6	7.8
Circumference, mm	25.0	24.8
Diameter, mm	7.9	7.9
Paper		
Porosity, sec.	16	27
Filter		
RTD, mm of H2O	100	101
Tipping Paper Length, mm	32	32
Filler		
Wt. of Tob., g (12.5% O.V.)	0.679	0.648
Oven Volatiles, %	14.6	13.9
Cigarette		
Ventilation, %	22	38
RTD, inches	4.8	4.3
Visibility, %	45	20

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TABLE VI

Comments:PROJECT STUDIO - MUL; 4-6mg TAR EXPECTED

	4703 CVA	4704 CVB
Smoke		
Butt Length, mm	35	35
FTC Tar, mg/cigt.	3.9	4.0
TPM, mg/cigt.	4.6	4.6
Nicotine, mg/cigt.	0.38	0.33
Water, mg/cigt.	0.34	0.28
Puffs/Cigt.	8.2	7.3
Filtration Eff., %		66
CO, mg/cigt.	3.2	4.2
NO, mg/cigt.	0.12	0.09
HCN, mg/cigt.	0.06	0.04
RCHO, mg/cigt.	0.31	0.30
Use Phase Puff Count		
Cigarette		
Total RTD, mm of H2O	102	105
Static Burn. Time, min	7.2	7.0
Paper		
Porosity, sec.	13	32
Filter		
RTD, mm of H2O	129	133
Tipping Paper Length,mm	32	32
Filler		
Wt. of Tob., g (12.5% O.V.)	0.614	0.576
Oven Volatiles, %	12.9	13.0
Cigarette		
Ventilation, %	61	59
RTD, inches	3.9	4.1

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